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SURFACTANT

#### (57) Abstract

The present invention relates to detergent compositions comprising a specific lipolytic enzyme and an alkyl poly glucoside surfactant. Such compositions provide improved overall detergency performance: reduced redeposition of greasy/oily substances on fabrics, dishware and hard surfaces thereby improving whiteness maintenance, cleaning, spotting, filming and stain removal performances.

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# DETERGENT COMPOSITIONS COMPRISING SPECIFIC LIPOLYTIC ENZYME AND ALKYL POLY GLUCOSIDE SURFACTANT

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#### TECHNICAL FIELD

The present invention relates to detergent compositions comprising a specific lipolytic enzyme and an alkyl poly glucoside surfactant.

#### BACKGROUND OF THE INVENTION

The inclusion of lipolytic enzyme (e.g. lipase) in detergent compositions for improved cleaning performance is known, e.g. enhancement of removal of triglycerides containing soils and stains from fabrics. Examples are US Patent 4,769,173, Cornelissen et al. issued August 29, 1989; US Patent 5,069,809, Lagerwaard et al., issued December 3, 1991; PCT application WO94/03578 and HAPPI (Household & Personal Products Industry) No. 28/1991.

In USP 4,769,173 is disclosed a certain class of lipases consisting of fungal lipases ex Humicola lanuginosa together with strong bleaching agents in detergent compositions.

An example of a fungal lipase in this patent is the lipase ex Humicola lanuginosa, available from Amano under the tradename Amano-CE.

In USP 5,069,809 is disclosed the combination of strong bleaching agents with a lipase enzyme produced by cloning the gene encoding the lipase produced by Humicola

lanuginosa and expressing the gene in Aspergillus oryzae as host for use in detergent compositions.

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In WO 94/03578 is disclosed an enzymatic detergent composition containing 10 to 20 000 LU (Lipolytic units) per gram of detergent composition of a lipase showing a substantial lipolytic activity during the main cycle of a wash process. This lipase is selected in particular on its inactivation behaviour with Diisopropyl Fluoro Phosphate (DFP).

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In spite of the large number of publications on lipase enzymes only the lipase derived from Humicola lanuginosa strain DSM 4106 and produced in Aspergillus oryzae as host has so far found wide-spread application as additive for fabric washing products. It is available from Novo Nordisk under the tradename Lipolase (TM). Gormsen and Malmos describe in HAPPI this enzyme with trademark "Lipolase" as being the first detergent lipase with a commercially relevant cost performance based on the use of recombinant DNA technology on an industrial scale.

In HAPPI is disclosed that Lipolase is the most effective during the drying step rather than the washing process itself. During the drying of the fabric, the conditions like water level are more favourable for lipolytic hydrolysis than during the actual wash cycle.

In order to optimize the stain removal performance of Lipolase, Novo Nordisk have made a number of variants.

As described in WO 92/05249 D96L variant of the native Humicola lanuginosa lipase improves the lard stain removal efficiency by a factor 4.4 over the wild-type lipase (enzymes compared in an amount ranging from 0.075 to 2.5 mg protein per liter).

In Research Disclosure No. 35944 published on March 10, 1994, by Novo Nordisk is disclosed that the lipase variant (D96L) may be added in an amount corresponding to 0.001-100mg (5-500.000 LU/1) lipase variant per liter of wash liquor.

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It is equally well recognised that lipolytic enzyme deactivation occurs in detergent formulations. The loss of activity of the enzyme is among others depending on the presence of adjunct detergent ingredients. One type of adjunct detergent ingredients is the surfactants.

A wide variety of detersive surfactants are known in the literature and in commercial practice. They perform a dual function within the detergent matrix. surfactant molecules reduce the interfacial tension between the soil and aqueous phase and thereby gradually remove the from the surface by a roll-up, emulsification or stain solubilisation mechanism. Anionic surfactants are particularly suitable for this function. Secondly, surfactant molecules keep the soil in suspension prevent redeposition onto the surface. Alkyl poly glucoside nonionic and anionic surfactants traditionally serve that purpose.

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Alkyl polyglucoside surfactants have been disclosed in U.S. Pat.Nos. 3,598,865; 3,721,633 and 3,772,269. patents also disclose processes for making polyglucoside surfactants and built liquid detergent compositions containing these surfactants. U.S. Pat.No. 3,219,656 discloses alkyl monoglucosides and suggests their utility as foam stabilizers for other surfactants. Various polyglucoside surfactant structures and processes making them are disclosed in U.S. Pat.Nos. 2,974,134; 3,640,998; 3,839,318; 3,314,936; 3,346,558; 4,011,389 and 4,223,129.

Alkyl polyglucoside surfactants have also been disclosed in combination with several cosurfactants in cleaning compositions. U.S. Pat.No. 4,396,520 discloses a detergent composition containing an alkyl polysaccharide surfactant and a calcium sensitive anionic detergent

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cosurfactant. U.S. Pat.No. 4,565,647 discloses a foaming composition containing an alkyl polysaccharide surfactant and a sulfate, sulfonate, and/or carboxylate cosurfactant. U.S. Pat. No. 4,599,188 discloses a foaming composition containing an alkyl polysaccharide surfactant, a sulfate, sulfonate and/or carboxylate cosurfactant, and an amide and/or amine oxide auxiliary foam booster. U.S. Pat.No. 4,732,704 discloses manual a dishwashing detergent composition containing an alkyl monoglucoside surfactant, an anionic surfactant of the sulfate or sulfonate type, and fatty acid alkanol amide. U.S. Pat. No. 4,839,098 discloses a manual dishwashing detergent composition containing an alkyl polyglucoside surfactant and a dialkyl sulfosuccinate.

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Alkyl poly glucoside surfactants are also described in WO 92/19711, WO 92/08439, DE 4 029 035, JP 3 163 198, JO 3 174 796, EP 216 301, EP 280 143, WO91/13096, and WO 92/19711.

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The overall performance of a detergent is judged by not only its ability to remove soils ans stains, e.g. greasy/oily soils, but also its ability to prevent redeposition of the soils, or the breakdown products of the soils or of any insoluble salt, on the article washed. Redeposition effects results in the articles being coated in an unseemly film, appearing streaked or being covered in visible spots which remain intact at the end of the wash process.

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Therefore, there remains a substantial technical challenge in formulating detergent compositions in such a manner to meet the consumer's need for superior overall detergency performances:

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The above objective has been met by detergent compositions including laundry, dishwashing and hard

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surface cleaner, containing a specific lipolytic enzyme and an alkyl poly glucoside surfactant.

Ιt has indeed been surprisingly found that the combination of a specific lipolytic enzyme with an alkyl 5 poly glucoside surfactant improves the overall detergency performance e.g. whiteness maintenance on fabrics reduced spotting, filming or redeposition of greasy/oily substances on dishware, hard surfaces and the like. It has been found that alkyl poly glucoside surfactants of the 10 type disclosed hereinafter provide a stabilising and/or performance boosting function for the specific lipolytic enzyme.

This finding allows either improved performance or a reduction of the surfactant/specific lipolytic enzyme levels while keeping the same detergency performance.

### 20 SUMMARY OF THE INVENTION

The present invention relates to detergent compositions comprising a specific lipolytic enzyme and an alkyl poly glucoside surfactant.

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#### DETAILED DESCRIPTION OF THE INVENTION

#### 30 Specific lipolytic enzyme

An essential component of the detergent composition according to the invention is a specific lipolytic enzyme.

In the present context, the term "lipolytic enzyme" is intended to indicate an enzyme exhibiting a lipid degrading capability, such as a capability of degrading a

triglyceride, a phospholipid, a wax-ester or cutin. The lipolytic enzyme may, e.g., be a lipase, a phospholipase, an esterase or a cutinase.

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The specific lipolytic enzymes suitable for the present invention are those lipolytic enzymes which provide a significantly improved whiteness maintenance performance when compared to an identical hydrolytic activity (same amount of LU per liter of wash solution) of the LipolaseTM enzyme.

10 The significant whiteness maintenance performance as used herein can be visually evaluated by expert graders using the 0→4 panel score units (PSU) Scheffé scale (0 stands for no difference and 4 represents a very large difference).

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The specific lipolytic enzyme suitable for the present invention is incorporated into the detergent composition in accordance with the invention at a level of from 50 LU to 8500 LU per liter wash solution. Preferably said lipolytic enzyme is present at a level of from 100 LU to 7500 LU per liter of wash solution. More preferably at a level of from 150 LU to 5000 LU per liter of wash solution.

Suitable specific lipolytic enzymes for use herein include those of bacterial and fungal origin. The lipolytic enzymes from chemically or genetically modified mutants are included herein.

Preferred lipolytic enzymes include variants of lipolytic enzymes producible by Humicola lanuginosa and Thermomyces lanuginosus, or by cloning and expressing the gene producing said variants responsible for into organism, e.g. Aspergillus oryzae as described in European Patent Application 0 258 068, incorporated herein by reference.

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Highly preferred lipolytic enzymes are variants of the native lipase derived from Humicola lanuginosa as described

in US Serial No. 08/341,826. Preferably the Humicola lanuginosa strain DSM 4106 is used. An example of said variants is D96L lipolytic enzyme.

By D96L lipolytic enzyme variant is meant the lipase variant as described in patent application WO 92/05249 viz. wherein the native lipase ex Humicola lanuginosa the aspartic acid (D) residue at position 96 is changed to Leucine (L). According to this nomenclature said substitution of aspartic acid to Leucine in position 96 is shown as: D96L.

To determine the activity of the enzyme D96L the standard LU assay was used (Analytical method, internal Novo Nordisk number AF 95/6-GB 1991.02.07). A substrate for D96L was prepared by emulsifying glycerine tributyrate (Merck) using gum-arabic as emulsifier. Lipase activity was assayed at pH 7 using pH stat. method.

One unit of lipase activity (LU/mg) is defined as the amount needed to liberate one micromole fatty acid per minute.

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#### Surfactant system

The detergent compositions according to the present invention comprise an alkyl poly glucoside surfactant of the formula:

wherein R is on the average a C<sub>10</sub> to C<sub>16</sub>, preferably C<sub>12</sub> to C<sub>14</sub>, alkyl, G is a moiety derived from a reducing saccharide containing fron 5 to 6 carbons atoms, preferably a glucose unit, and x is on the average from 1.0 to 3.0 preferably from about 1.1 to 1.5, and represent the average degree of polymerisation of the alkyl polysaccharide surfactant.

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For a particular alkyl polysaccharide molecule, x can only assume integral values. In any physical sample of alkyl polyglucoside surfactants, there will generally be molecules having different values of x. The physical sample can be characterized by the average value of x, which can assume non-integral values. In the specification, the values of x are to be understood to be average values.

polysaccharide hydrophilic portion The of the surfactant contains from about 1 to about 3, preferably 10 from 1.1. to about 1.5, saccharide units on the average. saccharide unit may galactoside, be glucoside, lactoside, fructoside, glucosyl, fructosyl, lactosyl and/or galactosyl units. Mixtures of these saccharide moieties may be used in the alkyl polysaccharide surfactant. Glucoside 15 the preferred saccharide moiety. Other saccharide moieties will act similarly, but because glucoside is the preferred saccharide moiety, the remaining disclosure will focus on the alkyl polyglucoside surfactant.

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The hydrophobic group on the alkyl polysaccharide is an alkyl group, either saturated or unsaturated, branched or unbranched, containing from about 10 to about 16 carbon atoms on the average. Preferably, the alkyl group is primarily a straight chain saturated  $C_{12}$  to  $C_{14}$  alkyl group.

U.S. Patent 4,565,647, Llenado, issued January 21, 1986, dicloses alkylpolysaccharides having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for

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the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding

The preferred alkylpolyglycosides have the formula

saccharide units.

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 $R^{2}O(C_{n}H_{2n}O)_{t}(glycosyl)_{x}$ 

wherein  $R^2$  is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon 15 atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or 20 alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, 25 preferably predominately the 2-position.

Said alkyl poly glucoside surfactants are comprised within the detergent compositions of the present invention at a level from 0.1 to 10%, preferably from 1 to 6%, more preferably from 2 to 5% by weight of total composition.

The objective of the washing process of soiled fabrics is to clean these, i.e. to remove soils and stains from the soiled clothes. However, as soon as the removed soils appear in the wash solution, they can redeposit onto the

fabrics being washed. Especially for white garments the redeposition of soil has a strong negative impact on the whiteness of the fabric. But also the brightness and freshness of colored fabrics is reduced by such redeposition.

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Whiteness maintenance is the monitoring of the whiteness of wash & wear fabrics over a number of washing cycles. A good performing detergent has a good whiteness maintenance profile, i.e. it ensures that the whiteness of washed fabrics is maintained at a high level during the complete life cycle of wearing & washing by preventing as much as possible the redeposition onto white fabrics of removed soils.

It has now been surprisingly found that the incorporation into detergents of the specific lipolytic enzymes with an alkyl poly glucoside surfactant according to the present invention delivers a significally superior benefit in whiteness maintenance performance.

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In addition, under hard surfaces cleaning and dishcare conditions the use of said specific lipolytic enzymes with an alkyl poly glucoside surfactant shows a reduced spotting, filming and/or redeposition of greasy/oily substances on dishes, plates, hard surfaces and the like.

#### Detergent components

The detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

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The cleaning compositions according to the invention can be liquid, paste, gels, bars, tablets, powder or granular forms. Granular compositions can also be in "compact" form, the liquid compositions can also be in a "concentrated" form.

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The compositions of the invention may for example, be formulated as hard surface cleaner, hand and dishwashing compositions, and hand machine laundry detergent compositions including laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics, rinse added fabric softener compositions.

When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other detergent compounds selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic compounds, bleaching agents, additional enzymes, suppressors, dispersants, lime-soap dispersants, release polymer, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components.

The compositions of the invention can also be used as detergent additive products. Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

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If needed the density of the granular laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 600 to 950 g/litre of composition measured at 20°C.

The "compact" form of the granular laundry detergent compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition.

In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition.

The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulphates and chlorides.

A preferred filler salt is sodium sulphate.

Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according the present invention will contain a lower amount of water, compared to conventional liquid detergents.

Typically the water content of the concentrated liquid detergent is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

#### Additional surfactant system

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The detergent compositions according to the present invention can additionally comprise a surfactant system

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wherein the surfactant can be selected from other nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

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The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 25% by weight of detergent compositions in accord with the invention.

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Preferred surfactant systems to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

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Polyethylene, polypropylene, and polybytylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation 20 products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straightchain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is 25 present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type Igepal<sup>TM</sup> CO-630, marketed by the GAF Corporation; 30 Triton  $^{\text{TM}}$  X-45, X-114, X-100 and X-102, all marketed by the Company. These surfactants are commonly Rohm & Haas referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

35 The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic

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surfactant of the nonionic surfactant systems of present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type Tergitol<sup>TM</sup> 15-S-9 (the condensation product of C11-C15 linear alcohol with 9 moles ethylene oxide),  $Tergitol^{TM}$  24-L-6 NMW (the condensation product of  $C_{12}-C_{14}$ alcohol with 6 moles ethylene oxide with a narrow molecular weight distribytion), both marketed by Union Corporation; Neodol<sup>TM</sup> 45-9 (the condensation product of  $C_{14}-C_{15}$  linear alcohol with 9 moles of ethylene oxide), Neodol<sup>TM</sup> 23-3 (the condensation product of  $C_{12}$ - $C_{13}$  linear alcohol with 3.0 moles of ethylene oxide), Neodol<sup>TM</sup> 45-7(the condensation product of  $C_{14}-C_{15}$  linear alcohol with 7 moles of ethylene oxide),  $Neodol^{TM}$  45-5 (the condensation product of  $C_{14}$ - $C_{15}$  linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, Kyro TM EOB (the condensation product of C13-C15 alcohol with ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA 030 or 050 (the condensation product of C12-C<sub>14</sub> alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will

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preferably have a molecular weight of from about 1500 to 1800 and will exhibit water insolubility. addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product retained is up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commerciallyavailable Pluronic $^{ ext{TM}}$  surfactants, marketed by BASF.

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Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic TM compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. preferred are  $C_8-C_{14}$  alkyl phenol ethoxylates having from 3 ethoxy groups and C8-C18 alcohol ethoxylates (preferably  $C_{10}$  avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.

$$R^{2} - C - N - Z,$$

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$$O R^{1}$$

wherein R<sup>1</sup> is H, or R<sup>1</sup> is C<sub>1-4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5-31</sub> hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R<sup>1</sup> is methyl, R<sup>2</sup> is a straight C<sub>11-15</sub> alkyl or C<sub>16-18</sub> alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

When included in such detergent compositions, the nonionic surfactant systems of the present invention act to improve the greasy/oily stain removal properties of such detergent compositions across a broad range of cleaning conditions.

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Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of  $C_8$ - $C_{20}$  carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous  $SO_3$  according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:

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wherein  $\mathbb{R}^3$  is a  $\mathbb{C}_8\text{-}\mathbb{C}_{20}$  hydrocarbyl, preferably an alkyl, or combination thereof,  $R^4$  is a  $C_1$ - $C_6$  hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. 10 salt-forming cations Suitable include metals such sodium, potassium, and lithium, and substituted unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R<sup>3</sup> is  $C_{10}-C_{16}$  alkyl, and  $R^4$  is methyl, ethyl or 15 Especially preferred are the methyl ester sulfonates wherein  $R^3$  is  $C_{10}$ - $C_{16}$  alkyl.

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Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids 20 of the formula  $ROSO_3M$  wherein R preferably is a  $C_{10}-C_{24}$ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a  $C_{10}-C_{20}$  alkyl component, more preferably a  $C_{12}-C_{18}$  alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or 25 substituted ammonium (e.g. methyl-, dimethyl-, trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived 30 alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the Typically, alkyl chains of  $C_{12}$ - $C_{16}$  are preferred for lower wash temperatures (e.g. below about 50°C) and  $C_{16-18}$  alkyl chains are preferred for higher wash temperatures (e.g. 35 above about 50°C).

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Other anionic surfactants useful for detersive purposes can also be included in the detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, substituted ammonium salts such as mono-, diand triethanolamine salts) of soap,  $C_8-C_{22}$  primary of secondary alkanesulfonates, C8-C24 olefinsulfonates, prepared by sulfonation of polycarboxylic acids pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179,  $C_8-C_{24}$  alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated  $C_{12}\text{-}C_{18}$  monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C6-C12 diesters), acyl sarcosinates, sulfates alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula  $RO(CH_2CH_2O)_k$ - $CH_2COO-M+$  wherein R is a  $C_8-C_{22}$  alkyl, k is an integer from 1 to 10, and M is a soluble saltforming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are described in "Surface Active Agents

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

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Highly preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula  $RO(A)_mSO3M$  wherein R is an unsubstituted  $C_{10}$ - $C_{24}$  alkyl or hydroxyalkyl group having a  $C_{10}$ - $C_{24}$  alkyl component, preferably a  $C_{12}$ - $C_{20}$ alkyl or hydroxyalkyl, more preferably  $C_{12}$ - $C_{18}$  alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., 10 sodium, potassium, lithium, calcium, magnesium, ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-15 ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and derived from alkylamines such those as ethylamine, diethylamine, triethylamine, mixtures thereof, and the 20 like. Exemplary surfactants are  $C_{1,2}-C_{1,8}$ polyethoxylate (1.0) sulfate  $(C_{12}-C_{18}E(1.0)M)$ , C12-C18 alkyl polyethoxylate (2.25) sulfate ( $C_{12}-C_{18}E(2.25)M$ ),  $C_{12}-C_{18}E(2.25)M$  $C_{18}$  alkyl polyethoxylate (3.0) sulfate ( $C_{12}-C_{18}E(3.0)M$ ), and  $C_{12}-C_{18}$  alkyl polyethoxylate (4.0) sulfate 25  $C_{18}E(4.0)M)$ , wherein M is conveniently selected from sodium and potassium.

When included therein, the detergent compositions of the present invention typically comprise from about 1% to 30 about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

The detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

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Cationic detersive surfactants suitable for use in the detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula:

$$[R^{2}(OR^{3})_{y}][R^{4}(OR^{3})_{y}]_{2}R^{5}N+X-$$

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wherein  $\mathbb{R}^2$  is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each  ${
m R}^3$  is selected from the group consisting of -CH2CH2-, - $CH_2CH(CH_3)$ -,  $-CH_2CH(CH_2OH)$ -,  $-CH_2CH_2CH_2$ -, and mixtures thereof; each  ${\sf R}^4$  is selected from the group consisting of  $C_1-C_4$  alkyl,  $C_1-C_4$  hydroxyalkyl, benzyl ring structures bv joining the two  $R^4$ groups, -CH2CHOH-CHOHCOR 6CHOHCH2OH wherein R6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0;  ${\bf R}^5$  is the same as  ${\bf R}^4$  or is an alkyl chain wherein the total number of carbon atoms of  ${\ensuremath{\mathtt{R}}}^2$ plus  $R^5$  is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

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Highly preferred cationic surfactants are the watersoluble quaternary ammonium compounds useful in the present composition having the formula:

$$R_1R_2R_3R_4N^+X^-$$
 (i)

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wherein  $R_1$  is  $C_8-C_{16}$  alkyl, each of  $R_2$ ,  $R_3$  and  $R_4$  is independently  $C_1-C_4$  alkyl,  $C_1-C_4$  hydroxy alkyl, benzyl, and  $-(C_2H_{40})_xH$  where x has a value from 2 to 5, and X is an anion. Not more than one of  $R_2$ ,  $R_3$  or  $R_4$  should be benzyl. The preferred alkyl chain length for  $R_1$  is  $C_{12}-C_{15}$  particularly where the alkyl group is a mixture of chain

lengths derived from coconut or palm kernel fat or is

derived synthetically by olefin byild up or OXO alcohols synthesis. Preferred groups for  $R_2R_3$  and  $R_4$  are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

5 Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are:

coconut trimethyl ammonium chloride or bromide; coconut methyl dihydroxyethyl ammonium chloride or bromide;

decyl triethyl ammonium chloride;
decyl dimethyl hydroxyethyl ammonium chloride or bromide;
C12-15 dimethyl hydroxyethyl ammonium chloride or bromide;

coconut dimethyl hydroxyethyl ammonium chloride or

bromide;
myristyl trimethyl ammonium methyl sulphate;
lauryl dimethyl benzyl ammonium chloride or bromide;
lauryl dimethyl (ethenoxy) 4 ammonium chloride or bromide;
choline esters (compounds of formula (i) wherein R1 is

20  $CH_2-CH_2-O-C-C_{12-14}$  alkyl and  $R_2R_3R_4$  are methyl).

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di-alkyl imidazolines [compounds of formula (i)].

25 Quaternary ammonium surfactants suitable for the present invention have the formula (I):

$$R_1$$
 $R_2$ 
 $R_3$ 
 $R_5$ 
 $R_5$ 
 $R_5$ 

Formula I

30 whereby R1 is a short chainlength alkyl (C6-C10) or alkylamidoalkyl of the formula (II):

Formula II

y is 2-4, preferably 3.

whereby R2 is H or a C1-C3 alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0,

whereby R3, R4 and R5 are either the same or different and can be either a short chain alkyl (C1-C3) or alkoxylated alkyl of the formula III,

whereby  $X^-$  is a counterion, preferably a halide, e.g. 10 chloride or methylsulfate.

Formula III

15 R6 is  $C_1-C_4$  and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined in formula I whereby

 $R_1$  is  $C_8$ ,  $C_{10}$  or mixtures thereof, x=0,

20 R<sub>3</sub>, R<sub>4</sub> = CH<sub>3</sub> and R<sub>5</sub> = CH<sub>2</sub>CH<sub>2</sub>OH.

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

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When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

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Ampholytic surfactants are also suitable for use in the detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines WO 97/43377

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in which the aliphatic radical can be straight— or branched—chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water—solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

of nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and

hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula

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## $R^3 (OR^4) \times N(R^5) 2$

wherein R<sup>3</sup> is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures therof containing from about 8 to about 22 carbon atoms; R<sup>4</sup> is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R<sup>5</sup> is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R<sup>5</sup> groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include  $C_{10}-C_{18}$  alkyl dimethyl amine oxides and  $C_8-C_{12}$  alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

The detergent composition of the present invention may 35 further comprise a cosurfactant selected from the group of primary or tertiary amines. Suitable primary amines for use herein include amines according to the formula  $R_1NH_2$  wherein  $R_1$  is a  $C_6-C_{12}$ , preferably  $C_6-C_{10}$  alkyl chain or  $R_4X(CH_2)_n$ , X is -O-,-C(0)NH- or -NH-,  $R_4$  is a  $C_6-C_{12}$  alkyl chain n is between 1 to 5, preferably 3.  $R_1$  alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C8-C10 oxypropylamine, octyloxypropylamine, 2-ethylhexyloxypropylamine, lauryl amido propylamine and amido propylamine.

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Suitable tertiary amines for use herein include tertiary amines having the formula  $\rm R_1R_2R_3N$  wherein R1 and R2 are  $\rm C_1-\rm C_8$  alkylchains or

$$-(c_{H_2}-c_{H_2}-c_{O})_{xH}$$

20 R<sub>3</sub> is either a C<sub>6</sub>-C<sub>12</sub>, preferably C<sub>6</sub>-C<sub>10</sub> alkyl chain, or R<sub>3</sub> is R<sub>4</sub>X(CH<sub>2</sub>)<sub>n</sub>, whereby X is -O-, -C(0)NH- or -NH-,R<sub>4</sub> is a C<sub>4</sub>-C<sub>12</sub>, n is between 1 to 5, preferably 2-3. R<sub>5</sub> is H or C<sub>1</sub>-C<sub>2</sub> alkyl and x is between 1 to 6.

R<sub>3</sub> and R<sub>4</sub> may be linear or branched; R<sub>3</sub> alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

Preferred tertiary amines are  $\rm R_1R_2R_3N$  where R1 is a C6-C12 alkyl chain, R2 and R3 are C1-C3 alkyl or

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$$-(c_{H_2}-c_{H}-c_{O})_{xH}$$

where R5 is H or CH3 and x = 1-2.

Also preferred are the amidoamines of the formula:

$$R_1 - C - NH - (CH_2) - N - (R_2)$$

wherein  $R_1$  is  $C_6-C_{12}$  alkyl; n is 2-4, preferably n is 3;  $R_2$  and  $R_3$  is  $C_1-C_4$ 

Most preferred amines of the present invention include 5 1-octylamine, 1-hexylamine, 1-decylamine, dodecylamine, C8-10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, bis(hydroxyethyl)amine, coco bis(hydroxyehtyl)amine, lauryl 10 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C8-10 amidopropyldimethylamine and C10 amidopropyldimethylamine. The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1dodecylamine. 15 Especially desirable dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

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#### Optional detergent ingredients:

Other detergent enzymes

- The detergent compositions can in addition to specific lipolytic enzyme enzymes further comprise one or more enzymes which provide cleaning performance and/or fabric care benefits.
- Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, other amylases, xylanases, other lipases, other esterases, other cutinases, pectinases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, ß-glucanases,

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arabinosidases, chondroitinase, laccase or mixtures thereof.

A preferred combination is a cleaning composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from Humicola insolens. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800. Other suitable cellulases are cellulases originated from Humicola insolens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo).

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromoperoxidase.

Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991.

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Said cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

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Preferred commercially available protease include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Nordisk under the tradename (Denmark), those sold Maxatase, Maxacal, Maxapem and Properase by Gist-Brocades, those sold Genencor International, and those sold under tradename Opticlean and Optimase by Solvay Enzymes. proteases described in patent applications EP WO91/06637 and WO95/10591 and USSN 08/322 676 can be included in the detergent composition of the invention. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

25 Other preferred enzymes that can be included in the detergent compositions of the present invention include other lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas Pseudomonas stutzeri group, such as ATCC 19.154, disclosed in British Patent 1,372,034. Suitable lipases 30 include those which show a positive immunological crossreaction with the antibody of the lipase, produced by the microorganism Pseudomonas fluorescent IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter 35 referred to as "Amano-P". Especially suitable lipases are lipases such as M1 Lipase $^{\mbox{\scriptsize R}}$  and Lipomax $^{\mbox{\scriptsize R}}$  (Gist-Brocades) and 5

 $Lipolase^{R}$  (Novo) which have found to be very effective when used in combination with the compositions of the present invention.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Suitable cutinases are described in WO 94/14963 and WO 94/14964. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

These other lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

15 Amylases  $(\alpha \text{ and/or } \beta)$  can be included for removal of carbohydrate-based stains. WO/94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO/94/18314, Genencor, published August 18, 1994 WO/95/10603, Novo Nordisk A/S, published April 20,1995. 20 Other amylases known for use in cleaning compositions include both lpha- and eta-amylases. lpha-Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; 25 285,123; 525,610; EP EP368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylase are stability-enhanced amylases including Purafact Ox  $Am^R$ described in WO 94/18314, published August 18, 1994 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed 30 in WO 95/10603, published April 95. Examples of commercial  $\alpha$ -amylases products are Termamyl®, Ban® ,Fungamyl® and Duramyl® all available from Novo Nordisk A/S Denmark. W095/26397 describes other suitable amylases : lphaamylases characterised by having a specific activity at 35 least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in

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the range of 8 to 10, measured by the Phadebas®  $\alpha$ -amylase activity assay. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition. The enzymes can be added as single ingredients (prills, granulates, stabilised liquids, etc...) or as mixture of of two or more enzymes (e.g. cogranulates).

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Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in the copending European patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

#### Color care benefits

Technologies which provide a type of color care benefit can be also included. Examples of these technologies are metallo catalysts for color maintenance. Such metallo catalysts are described in the European patent EP 0 596 184 and in the copending European Patent Application No. 94870206.3.

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#### Bleaching agent

Bleach systems that can be included in the detergent compositions of the present invention include bleaching agents such as PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can include one or more oxygen bleaching agents and,

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depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

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The bleaching agent component for use herein can be any of the bleaching agents useful for detergent compositions including oxygen bleaches as well as others known in the art.

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The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and 15 salts thereof. Suitable examples of this class of agents magnesium monoperoxyphthalate hexahydrate, magnesium salt of meta-chloro perbenzoic acid, 4nonylamino-4-oxoperoxybytyric acid and diperoxydodecanedioic 20 acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described 25 in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo sulphonamides. Such materials are normally added at 0.5-10%by weight of the finished product, preferably 1-5% by weight.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetylethylenediamine (TAED), nonanoyloxybenzene-

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sulfonate (NOBS, described in US 4,412,934), 3, 5, trimethylhexanoloxybenzenesulfonate (ISONOBS, described in 120,591), pentaacetylglucose (PAG) or Phenolsulfonate N-nonanoyl-6-aminocaproic ester of acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a active bleaching as the species, improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Copending European Patent Application No. 91870207.7.

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Ιt has been found that combination of specific lipolytic enzyme with a bleaching agent and especially with nonanoyloxybenzene-sulfonate (NOBS) and Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS) bleach activator, as reduce the spotting, filming and/or redeposition thereby enhancing the whiteness maintenance and the greasy/oily stain removal performance.

Useful bleaching agents, including peroxyacids and 20 bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in co-pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 WO95/27775. 25

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the

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sulfonated zinc and/or aluminum phthalocyanines. materials can be deposited upon the substrate during the washing process. Upon irradiation with light, presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% about 1.25%, by weight, of sulfonated phthalocyanine.

#### Builder system

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The compositions according to the present invention may further comprise a builder system.

Any conventional builder system is suitable for use 20 including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine 25 pentamethylenephosphonic acid. Phosphate builders as sodium tripolyphosphate can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate (Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives

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thereof as disclosed in Belgian Patent Nos. 831,368, 821,370. Polycarboxylates containing two 821,369 and carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as as succinate derivatives such carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups 20 include oxydisuccinates disclosed in British Patent No. 1,1,2,2-ethane tetracarboxylates, 1,261,829, propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate disclosed in British Patent Nos. 1,398,421 and 1,398,422 25 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

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Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis, cis, cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran -tetracarboxylates, 1,2,3,4,5,6-hexane -hexacar-boxylates and and carboxymethyl derivatives of polyhydric alcohols

such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

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of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid.

A suitable chelant for inclusion in the detergent 15 compositions in accordance with the invention ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS 20 free acid form and the sodium compounds are the magnesium salt thereof. Examples of such preferred sodium salts of EDDS include Na<sub>2</sub>EDDS and Na<sub>4</sub>EDDS. Examples of such preferred magnesium salts of EDDS include MgEDDS  ${
m Mg}_2{
m EDDS}$ . The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention. 25

Preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid.

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Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

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Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

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Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

#### Suds suppressor

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Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. generally represented by Silicones can be alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially nonsurface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially

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available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alcanols. Suitable 2-alkyl-alkanols are 2-bytyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil<sup>R</sup>.

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The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

#### 20 Others

Other components used in detergent compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616.

Other suitable water soluble encapsulating materials comprise dextrins derived from ungelatinized starch acidesters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrins are, preferably, prepared from such starches as waxy maize, waxy sorghum,

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sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as carboxymethylcellulose methylcellulose, and hydroxyethylcellulose, and homoor co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

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Preferred optical brighteners are anionic character, examples of which are disodium 4,4'-bis-(2diethanolamino-4-anilino -s- triazin-6-ylamino) stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4anilino-s-triazin-6-ylamino-stilbene-2:2' - disulphonate, 4,4' disodium bis-(2,4-dianilino-s-triazin-6ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' bis-(2,4-dianilino-s-tri-azin-6 ylamino) stilbene-2sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium 4,4'bis(2anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6ylami-no)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are the specific brighteners of copending European Patent application No. 95201943.8.

Other useful polymeric materials are the polyethylene 5 glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and previously mentioned homoor co-polymeric polycarboxylate salts are valuable for improving whiteness 10 fabric maintenance, ash deposition, and performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula

25  $(CH_3(PEG)_{43})_{0.75}(POH)_{0.25}[T-PO)_{2.8}(T-PEG)_{0.4}]T(PO-H)_{0.25}((PEG)_{43}CH_3)_{0.75}$ 

where PEG is  $-(OC_2H_4)O-$ , PO is  $(OC_3H_6O)$  and T is  $(pcOC_6H_4CO)$ .

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-

capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

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The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

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Is is well known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the amylase enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

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### Softening agents

Fabric softening agents can also be incorporated into laundry detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as

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disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

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Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added either spray-dried or as a dry mixed component. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

#### Dye transfer inhibition

The detergent composition of the present invention can also include compounds for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

# 30 Polymeric dye transfer inhibiting agents

The detergent compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into detergent compositions in order to

inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinyloxazolidones and polyvinylimidazoles or mixtures thereof.

Addition of such polymers also enhances the performance of the enzymes according the invention.

### a) Polyamine N-oxide polymers

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The polyamine N-oxide polymers suitable for use contain units having the following structure formula:

wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

A is NC, CO, C, -O-,-S-, -N-; x is O or 1;
R are aliphatic, ethoxylated aliphatics, aromatic,
heterocyclic or alicyclic groups or any
combination thereof whereto the nitrogen of the N-O
group can be attached or wherein the nitrogen of
the N-O group is part of these groups.

The N-O group can be represented by the following general structures :

5 O O (R1) 
$$x - N - (R2) y = N - (R1) x$$
 (R3)  $z$ 

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wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

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Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-0 functional group is part of said R group.

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Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 25 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of Noxidation. Preferably, the ratio of amine to amine N-oxide 30 is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine Noxide and the other monomer type is either an amine N-oxide 35 or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferred PKa < 6.

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The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

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# b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

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The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4.

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#### c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially vailable from ISP Corporation, New York, NY and Montreal, Canada under the 15 product names PVP K-15 (viscosity molecular weight 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90(average molecular weight of 360,000). Other polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to persons skilled detergent field (see for example EP-A-262,897 and EP-A-256,696).

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#### d) Polyvinyloxazolidone:

The detergent compositions of the present invention may also utilize polyvinyloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinyloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

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#### e) Polyvinylimidazole:

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles have an average about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

### f) Cross-linked polymers:

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Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups n the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling.

Such cross-linked polymers are described in the co-25 pending patent application 94870213.9

#### Method of washing

The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid composition may be added.

The process described herein comprises contacting fabrics with a laundering solution in the usual manner and exemplified hereunder.

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The process of the invention is conveniently carried out in the course of the cleaning process. The method of cleaning is preferably carried out at 5 °C to 95 °C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 11. Typically, the following dosing quantities under european and american washing conditions are respectively: 4-10 g and 1-2 g of the detergent composition per litre.

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A preferred machine dishwashing method comprises treating soiled articles with an aqueous solution of the machine diswashing or rinsing composition. A conventional effective amount of the machine dishwashing composition means from 8-60 g of product dissolved or dispersed in a wash volume from 3-10 litres.

According to a manual dishwashing method, soiled dishes are contacted with an effective amount of the diswashing composition, typically from 0.5-20g (per 25 dishes being treated). Preferred manual dishwashing methods include the application of a concentrated solution to the surfaces of the dishes or the soaking in large volume of dilute solution of the detergent composition.

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The compositions of the invention may also be formulated as hard surface cleaner compositions.

The following examples are meant to exemplify 30 compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

In the detergent compositions, the level of the enzymes other than the specific lypolytic enzyme of the present invention, are expressed in % pure enzyme by weight of total composition and the abbreviated component identifications have the following meanings:

LAS	: Sodium linear $C_{12}$ alkyl benzene sulphonate
TAS	: Sodium tallow alkyl sulphate
XYAS	: Sodium $C_{1X}$ - $C_{1Y}$ alkyl sulfate
SAS	: $C_{12}-C_{14}$ secondary (2,3) alkyl sulfate in the form of the sodium salt.
AE	: Alcohol ethoxylated
APG	: Alkyl poly glucoside surfactant according to the present invention
AEC	: Alkyl ethoxycarboxylate surfactant of formula ${\it C}_{12}$ ethoxy (2) carboxylate.
SS	: Secondary soap surfactant of formula 2-bytyl octanoic acid
25EY	: A C <sub>12-</sub> C <sub>15</sub> predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
45EY	: A $C_{14}$ - $C_{15}$ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
XYEZS	: $C_{1X}$ - $C_{1Y}$ sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole

Nonionic : C<sub>13</sub>-C<sub>15</sub> mixed

ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafac LF404 by

BASF Gmbh

CFAA : C<sub>12</sub>-C<sub>14</sub> alkyl N-methyl glucamide

TFAA : C<sub>16</sub>-C<sub>18</sub> alkyl N-methyl glucamide.

Silicate : Amorphous Sodium Silicate (SiO<sub>2</sub>:Na<sub>2</sub>O

ratio = 2.0

NaSKS-6 : Crystalline layered silicate of

formula  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>

Carbonate : Anhydrous sodium carbonate

Metasilicate : Sodium metasilicate (SiO<sub>2</sub>:Na<sub>2</sub>O ratio =

2.0)

Phosphate or STPP : Sodium tripolyphosphate

MA/AA : Copolymer of 1:4 maleic/acrylic acid,

average molecular weight about 80,000

PA30 : Polyacrylic acid of average molecular

weight of approximately 8,000.

Terpolymer : Terpolymer of average molecular

weight approx. 7,000, comprising acrylic:maleic:ethylacrylic acid monomer units at a weight ratio of

60:20:20

480N : Random copolymer of 3:7

acrylic/methacrylic acid, average

molecular weight about 3,500.

Polyacrylate

: Polyacrylate homopolymer with an average molecular weight of 8,000 sold under the tradename PA30 by BASF GmbH

Zeolite A

: Hydrated Sodium Aluminosilicate of formula Na<sub>12</sub>(AlO<sub>2</sub>SiO<sub>2</sub>)<sub>12</sub>. 27H<sub>2</sub>O having a primary particle size in the range from 1 to 10 micrometers

Citrate

: Tri-sodium citrate dihydrate

Citric

: Citric Acid

Perborate

: Anhydrous sodium perborate monohydrate bleach, empirical formula NaBO2.H2O2

PB4

: Anhydrous sodium perborate tetrahydrate

Percarbonate

: Anhydrous sodium percarbonate bleach of empirical formula 2Na<sub>2</sub>CO<sub>3</sub>.3H<sub>2</sub>O<sub>2</sub>

TAED

: Tetraacetyl ethylene diamine.

NOBS

: Nonanoyloxybenzene-sulfonate.

NACA-OBS

: Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid.

Paraffin

: Paraffin oil sold under the tradename Winog 70 by Wintershall.

Pectinase

: Pectolytic enzyme sold under the tradename Pectinex AR by Novo Nordisk A/S.

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Xylanase

: Xylanolytic enzyme sold under the tradenames Pulpzyme HB or SP431 by Novo Nordisk A/S or Lyxasan by Gist-Brocades or Optipulp or Xylanase by Solvay.

Protease

: Proteolytic enzyme sold under the tradename Savinase, Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446.

Amylase

: Amylolytic enzyme sold under the tradename Purafact Ox AmR described in WO 94/18314, sold by Genencor; Termamyl®, Fungamyl® and Duramyl® all available from Novo Nordisk A/S and those described in Wo95/26397.

Enzyme

Specific Lipolytic : Lipolytic enzyme sold under the tradename Lipolase Ultra by Novo

Nordisk A/S.

Peroxidase

: Peroxidase enzyme.

Cellulase

: Cellulosic enzyme sold under the tradename Carezyme or Celluzyme by

Novo Nordisk A/S.

CMC

: Sodium carboxymethyl cellulose

HEDP

: 1,1-hydroxyethane diphosphonic acid

DETPMP

: Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060.

PAAC

: pentaamine acetate cobalt (III) sal.

BzP

: Benzoyl peroxide.

PVP

: Polyvinyl pyrrolidone polymer.

**PVNO** 

: Poly(4-vinylpyridine)-N-Oxide.

LSD

: C<sub>16</sub>-C<sub>18</sub> dimethyl amine oxide, C<sub>12</sub>-C<sub>18</sub> alkyl ethoxysulfates etoxylation degree 1-5, and the C<sub>13</sub>-C<sub>15</sub> ethoxylated alcohols 12 or 30, sold under the trade names Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

SRP

: Sulfonated poly-ethoxy/propoxy end capped ester oligomer and/or short block polymer synthetised from Dimethyl-terephtalate, 1,2 propylene Glycol, methyl capped PEG or sulfoethoxylate.

EDDS

: Ethylenediamine -N, N'- disuccinic acid, [S,S] isomer in the form of the sodium salt.

Granular Suds Suppressor : 12% Silicone/silica, 18% stearyl alcohol,70% starch in granular form

SCS

: Sodium cumene sulphonate

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Sulphate : Anhydrous sodium sulphate.

HMWPEO : High molecular weight polyethylene

oxide

PGMS : Polyglycerol monostearate having a

tradename of Radiasurf 248

TAE 25 : Tallow alcohol ethoxylate (25)

PEG(-6) : Polyethylene glycol (having a

molecular weight of 600).

BTA : Benzotriazole

Bismuth nitrate : Bismuth nitrate salt

NaDCC : Sodium dichloroisocyanurate

KOH : 100% Active solution of Potassium

Hydroxide

pH : Measured as a 1% solution in

distilled water at 20°C.

#### Example 1

Granular fabric cleaning compositions in accord with the invention were prepared as follows:

	I	II	III	IV	v
APG	3.0	5.0	8.0	8.0	4.0
LAS	20.0	16.0	14.0	14.0	18.0
Phosphate	23.0	23.0	22.0	22.0	23.0
Carbonate	23.0	23.0	22.0	22.0	23.0
Silicate	14.0	14.0	14.0	14.0	14.0
Zeolite A	8.2	8.2	8.2	8.2	8.2

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DETPMP	0.4	0.4	0.4	0.4	0.4
Sodium sulfate	5.5	5.5	5.5	5.5	5.5
Amylase	0.005	0.02	0.01	0.01	0.02
Protease	0.01	0.02	0.01	0.005	-
Pectinase	0.02	_	_	_	_
Xylanase	_	_	0.01	0.02	_
Specific lipolytic enzyme	0.005	0.01	0.002	0.005	0.003
Cellulase	0.001	_	-	0.001	
Water & minors		Uŗ	to 10	0 %	

# Example 2

Granular fabric cleaning compositions in accord with the invention were prepared as follows:

	I	II	III	IV	v
APG	3.0	10.0	5.0	5.0	5.0
LAS	12.0	10.0	12.0	12.0	12.0
Zeolite A	23.0	23.0	26.0	26.0	23.0
SS	4.0	4.0	4.0	4.0	4.0
SAS	5.0	5.0	5.0	5.0	5.0
Citrate	5.0	5.0	5.0	5.0	5.0
Sodium Sulfate	17.0	17.0	17.0	28.0	17.0
Perborate	16.0	16.0	16.0	_	16.0
TAED	5.0	-	-		5.0
NOBS	_	3.0	_	_	_
NACA-OBS	_	_	4.0	_	2.5
Protease	0.06	0.03	0.02	0.08	_
Specific lipolytic	0.004	0.005	0.008	0.10	0.002
enzyme					
Amylase	0.01	0.015	0.01	0.02	0.005
Water & minors		U	to 100		

# Example 3

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Granular fabric cleaning compositions in accord with the invention which are especially useful in the laundering of coloured fabrics were prepared as follows:

	I	II	III
APG	3.0	10.0	5.0
LAS	11.4	10.7	_
TAS	1.8	2.4	_
TFAA	_	_	4.0
45AS	3.0	3.1	10.0
45E7	4.0	4.0	_
25E3S	-	_	3.0
68E11	1.8	1.8	
25E5	-	_	8.0
Citrate	14.0	15.0	7.0
Carbonate	-	-	10.0
Citric	3.0	2.5	3.0
Zeolite A	32.5	30.0	25.0
Na-SKS-6	-	-	9.0
MA/AA	5.0	5.0	5.0
DETPMP	1.0	0.2	0.8
Protease	0.02	0.02	0.01
Specific lipolytic enzyme	0.002	0.008	0.002
Amylase	0.01	-	_
Silicate	2.0	2.5	-
Sulphate	3.5	5.2	3.0
PVP	0.3	0.5	_
Poly (4-vinylpyridine)-N-	-	-	0.2
<pre>oxide/copolymer of vinyl-</pre>			
imidazole and vinyl-			
pyrrolidone			
Perborate	0.5	1.0	-
Peroxidase	0.01	0.01	-
Phenol sulfonate	0.1	0.2	
Water/Minors		Up to 100%	

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Example 4

Granular fabric cleaning compositions in accord with the invention were prepared as follows:

	I	II	III	IV
APG	8.0	8.0	10.0	4.0
LAS	6.5	8.0	9.0	8.0
25AE3S	_	_	1.0	1.0
AS	15.0	18.0	7.5	7.0
23E6.5	_	_	2.0	3.0
Zeolite A	26.0	22.0	24.0	28.0
Sodium nitriloacetate	5.0	5.0	-	_
PVP	0.5	0.7	_	_
NOBS	-	-	3.0	_
DTPA	_	_	0.3	_
Perborate	0.5	1.0	2.0	1.0-
Boric acid	4.0	-	-	_
Phenol sulfonate	0.1	0.2	-	-
PEG	_	-	1.0	1.0
Polyacrylate	_	_	3.0	3.0
Protease	0.06	0.02	0.02	0.01
Silicate	5.0	5.0	1.0	1.0
Carbonate	15.0	15.0	15.0	30.0
Peroxidase	0.1	0.1	_	_
Pectinase	0.02	-	_	_
Cellulase	0.005	0.002	0.0005	0.002
Specific lipolytic enzyme	0.001	0.0005	0.001	0.001
Amylase	0.01	0.01	0.01	-
SRP	-	-	0.2	0.2
Sulfate	_	-	19.5	6.5
Water/minors		Up to	100%	

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# Example 5

A compact granular fabric cleaning composition in accord with the invention was prepared as follows:

	I	II
APG	4.0	6.0
LAS	0.0	8.0
TAS	0.0	2.0
45AS	8.0	0.0
25E3S	2.0	0.5
25E5	3.0	5.0
25E3	3.0	0.0
TFAA	2.5	0.0
Coco-alkyl-dimethyl hydroxy-	0.0	1.0
ethyl ammonium chloride		
Zeolite A	17.0	15.0
NaSKS-6	12.0	10.0
Citric acid	3.0	2.0
Carbonate	7.0	8.0
MA/AA	5.0	1.0
CMC	0.4	0.4
Poly (4-vinylpyridine)-N-oxide/	0.2	0.0
copolymer of vinylimidazole and		
vinylpyrrolidone		
Protease	0.05	0.03
Specific lipolytic enzyme	0.002	0.004
Cellulase	0.001	0.001
Amylase	0.01	0.006
TAED	6.0	3.0
Percarbonate	18.0	20.0
NACA-OBS	0.0	3.0
EDDS	0.3	0.2
Granular suds suppressor	3.5	3.0
water/minors/sulfate	Up to	100%

# Example 6

A granular fabric cleaning compositions in accord with the invention which provide "softening through the wash" capability were prepared as follows:

	I	II
APG	5.0	5.0
45AS	_	8.0
LAS	5.6	-
68AS	1.3	-
45E7	3.5	-
25E3	-	4.0
Coco-alkyl-dimethyl hydroxy-	1.4	1.0
ethyl ammonium chloride		
Citrate	5.0	3.0
Na-SKS-6	-	10.0
Zeolite A	15.0	12.0
MA/AA	4.0	4.0
DETPMP	0.4	0.4
Perborate	15.0	_
Percarbonate	_	14.0
TAED	5.0	3.0
NACA-OBS	_	2.0
Smectite clay	10.0	8.0
HMWPEO	_	0.1
Protease	0.02	0.01
Specific lipolytic enzyme	0.0005	0.01
Amylase	0.03	0.005
Cellulase	0.001	-
Silicate	3.0	5.0
Carbonate	10.0	7.0
Granular suds suppressor	1.0	4.0
CMC	0.2	0.1
Water/minors/sulfate	Up to	100%

### Example 7

Heavy duty liquid fabric cleaning compositions suitable for use in the pretreatment of stained fabrics, and for use in a machine laundering method, in accord with the invention were prepared as follows:

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	I	II	III	IV	v
APG	3.0	3.0	6.0	6.0	10.0
24AS	20.0	17.0	15.0	15.0	12.0
SS	5.0	5.0	5.0	5.0	5.0
Citrate	1.0	1.0	1.0	1.0	1.0
12E <sub>3</sub>	13.0	13.0	13.0	13.0	13.0
Monoethanolamine	2.5	2.5	2.5	2.5	2.5
Protease	0.005	0.03	0.02	0.04	0.01
Specific Lipolytic	0.008	0.01	0.007	0.0005	0.004
enzyme					
Amylase	0.005	0.005	0.001	0.01	0.004
Cellulase	0.04	_	0.01	_	_
Pectinase	0.02	0.02	~	_	_
Water/propylene glycol/ethanol (100:1:1)					

# Example 8

Heavy duty liquid fabric cleaning compositions in accord with the invention were prepared as follows:

	I	II	III	IV
APG	3.0	3.0	6.0	6.0
LAS acid form	-	-	20.0	_
C <sub>12-14</sub> alkenyl succinic acid	3.0	8.0	10.0	-
Citric acid	10.0	15.0	2.0	2.0
25AS acid form	8.0	8.0	-	12.0
25AE2S acid form	-	3.0	-	4.0
25AE7	••	8.0	-	6.0
25AE3	8.0	_	-	_
CFAA	-	-	4.0	6.0
DETPMP	0.2	-	1.0	1.0
Fatty acid	-	-	-	10.0
Oleic acid	1.8	_	1.0	_
Ethanol	4.0	4.0	6.0	2.0
Propanediol	2.0	2.0	6.0	10.0
Protease	0.02	0.02	0.02	0.01

Specific lipolytic enzyme	0.005	0.01	0.005	0.002	
Coco-alkyl dimethyl	_		3.0	_	
hydroxy ethyl ammonium					
chloride					
Smectite clay	_	-	5.0	_	
SRP	_	_	0.2	0.1	
PVP	1.0	2.0	_	_	
Perborate	-	1.0	_	_	
Phenol sulphonate	~	0.2	_	_	
Peroxidase	_	0.01	_	_	
NaOH	Up to pH 7.5				
Waters/minors		Up to 1	00%		

### Example 9

Heavy duty liquid fabric cleaning compositions in accord with the invention were prepared as follows:

	I	II	III
APG	5.0	8.0	3.0
Mono ethanol amine	1.0	1.1	0.7
C12HLAS	_	-	9.6
C25AE2.5S	19.0	19.0	13.8
Propane diol	6.2	6.3	4.9
23 <b>E</b> 9	2.0	2.0	2.2
Sodium toluene sulfonate	2.5	2.8	1.5
NaOH	3.4	3.1	6.6
Polyhydroxy fatty acid	3.5	3.5	_
amide			
Citric acid	3.0	3.0	7.1
Fatty acid	2.0	2.0	_
Specific lipolytic enzyme	0.004	0.01	0.01
Borax	2.5	2.5	2.2
Ethanol	3.4	3.4	1.9
SRP	0.2	0.1	0.3
E15-18 ethoxylated	1.2	1.3	1.2
tetraethylene pentaimine			

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Glycerine - 3.0 Water & Minors Up to 100%

### Example 10

Bleach-containing non-aqueous fabric cleaning 5 composition in accord with the invention was prepared as follows:

C12-15 alkyl ether (EO=3) sulfate Na Salt	14.0
CFAA	8.0
C12-14, Eo=5 alcohol ethoxylate	14.0
N-butoxy propoxy propanol	20.0
APG	4.0
Perfume	0.7
Topped palm kernel fatty acid Na salt	5.7
Trisodium citrate	1.9
Sodium percarbonate	9.4
Sodium carbonate	7.5
Sodium hydroxyethyl diphosphonate Na salt	1.7
[4-[N-nonanoyl-6-aminohexanoyloxy]benzene	4.7
sulfonate]2 Ca salt	
Brightener	0.2
Silicone oil DB-10	0.5
Specific lipolytic enzyme	0.005
Amylase	0.05
Protease	0.01
Cellulase	0.001
Minors	Up to 100%

### 10 Example 11

The following rinse added fabric softener composition, in accord with the invention, was prepared (parts by weight).

APG	4.0
Softener active	24.5
PGMS	2.0
TAE 25	1.5
Specific lipolytic enzyme	0.001
Cellulase	0.001
HCL	0.12
Antifoam agent	0.019
Blue dye	80ppm
CaCl <sub>2</sub>	0.35
Perfume	0.90

# Example 12

Syndet bar fabric cleaning compositions in accord with the invention were prepared as follows:

	I	II	III	IV
APG	4.0	4.0	4.0	4.0
C12-16 alkyl sulfate, Na	20.0	20.0	20.0	20.0
CFAA	5.0	5.0	5.0	5.0
C11-13 alkyl benzene	9.0	9.0	9.0	9.0
sulphonate, Na				
Sodium carbonate	25.0	25.0	25.0	25.0
Sodium pyrophosphate	7.0	7.0	7.0	7.0
Sodium tripolyphosphate	7.0	7.0	7.0	7.0
Zeolite A	5.0	5.0	5.0	5.0
Carboxymethylcellulose	0.2	0.2	0.2	0.2
Polyacrylate (MW 1400)	0.2	0.2	0.2	0.2
Coconut monethanolamide	5.0	5.0	5.0	5.0
Specific lipolytic enzyme	0.01	0.01	0.005	0.001
Protease	0.3	-	0.5	0.05
Brightener, perfume	0.2	0.2	0.2	0.2
CaSO4	1.0	1.0	1.0	1.0
MgSO4	1.0	1.0	1.0	1.0
Water	4.0	4.0	4.0	4.0

Filler\* : balance to 100%

\*Can be selected from convenient materials such as CaCO3, talc, clay (Kaolinite, Smectite), silicates, and the like.

### 5 Example 13

The following compact high density (0.96 Kg/l) dishwashing detergent compositions I to VI were prepared in accord with the invention:

	I	II	III	IV	v	VI
APG	4.0	2.0	2.0	4.0	8.0	8.0
STPP	-	_	46.0	35.0	-	-
Citrate	30.0	17.05	-	-	15.0	25.0
Carbonate	-	17.50	-	14.0	15.0	22.0
Silicate	30.0	14.81	20.36	14.81	13.00	_
Metasilicate	-	2.50	2.50	_	-	-
Perborate	1.94	9.74	7.79	14.28	9.00	-
PB4	8.56	-	_	-	_	-
Percarbonate	-	-	-	-	-	6.70
Nonionic	1.50	2.00	1.50	1.50	2.00	2.60
TAED	4.78	-	2.39	_	2.0	4.00
NOBS	-	4.00	-	-	_	4.0
NACA-OBS	_	-	2.50	_	-	_
HEDP	0.83	1.00	0.46	-	0.83	_
DETPMP	0.65	0.65	_	_	-	_
PAAC	-	_	-	0.20	-	-
BzP	-	-	-	4.44	-	-
Paraffin	0.50	0.50	0.50	0.50	-	0.20
Protease	0.075	0.05	0.10	0.10	0.08	0.01
Specific	0.0005	0.001	0.001	0.005	0.0004	0.001
lipolytic enzyme						
Amylase	0.01	0.005	0.015	0.015	0.005	0.0025
BTA	0.30	0.30	0.30	0.30	_	-
Bismuth Nitrate	-	0.30	_	-	_	-
PA30	4.02	-	_	-	_	-
Terpolymer	_		_	4.00	-	-

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480N	-	6.00	2.77	-	6.00	_
LSD	-	_	2.5	-	_	10.0
Sulphate	5.0	17.0	3.0	_	23.0	1.00
pH (1% solution)	10.80	11.00	10.90	10.80	10.90	9.60
Water and minors			Up t	:0 100%		

# Example 14

5 The following granular dishwashing detergent compositions examples I to IV of bylk density 1.02Kg/L were prepared in accord with the invention:

	I	II	III	IV	v	VI
APG	4.0	4.0	4.0	6.0	6.0	8.0
STPP	25.0	25.0	25.0	26.00	30.0	26.70
Carbonate	27.0	27.0	27.0	22.00	25.00	2.80
Silicate	7.40	7.40	7.40	12.00	8.00	20.34
Perborate	4.40	4.40	4.40		4.40	_
NaDCC	-	_	-	2.00	_	1.50
Nonionic	0.75	0.75	0.75	1.90	1.20	0.50
TAED	1.00	1.00	_	_	1.00	_
PAAC	_	_	0.004	_	-	
BzP	_	1.40	-	_	_	_
Paraffin	0.25	0.25	0.25	-	_	_
Protease	0.05	0.05	0.05	_	0.1	-
Specific	0.005	0.001	0.001	0.0005	0.0008	0.001
lipolytic enzyme						
Amylase	0.003	0.001	0.01	0.02	0.01	0.015
BTA	0.15	_	0.15	-	_	_
LSD	-	-	_	5.0	_	10.0
Sulphate	18.0	18.0	20.0	21.0	12.0	_
pH (1% solution)	10.80	10.80	10.80	10.70	10.70	12.30
Water and minors			Up	to 100%		

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# Example 15

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The following detergent composition tablets of 25g weight were prepared in accord with the present invention by compression of a granular dishwashing detergent composition at a pressure of  $13KN/cm^2$  using a standard 12 head rotary press:

	I	II	III
APG	5.0	5.0	5.0
STPP	-	42.0	42.0
Citrate	25.00	-	-
Carbonate	_	5.00	•••
Silicate	25.00	14.80	25.00
Protease	0.03	0.075	0.01
Specific lipolytic	0.005	0.001	0.0005
enzyme			
Amylase	0.01	0.005	0.001
Perborate	1.56	7.79	_
PB4	6.92	••	11.40
Nonionic	1.20	2.00	1.10
TAED	4.33	2.39	0.80
HEDP	0.67	_	-
DETPMP	0.65	_	-
Paraffin	0.42	0.50	_
BTA	0.24	0.30	-
PA30	3.2	_	-
LSD	10.0		-
Sulphate	10.0	10.5	3.20
pH (1% solution)	10.60	10.60	11.00
Water and minors		Up to 100%	

### Example 16

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The following liquid dishwashing detergent compositions in accord with the present invention I to II, of density 1.40Kg/L were prepared:

I

II

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APG	4.0	4.0
STPP	33.30	20.00
Carbonate	2.70	2.00
Silicate	-	4.40
NaDCC	1.10	1.15
Nonionic	2.50	1.00
Paraffin	2.20	_
Protease	0.03	0.02
Specific lipolytic enzyme	0.005	0.0025
480N	0.50	4.00
КОН	_	6.00
LSD	2.0	
Sulphate	1.60	-
pH (1% solution)	9.10	10.00
Water and nimors	Up to 10	0 %

# Example 17

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The following liquid hard surface cleaning compositions were prepared in accord with the present invention:

	I	II	III	IV	v	VI
Specific lipolytic	0.01	0.002	0.005	0.02	0.001	0.005
enzyme						
Protease	0.05	0.01	0.02	0.03	0.005	0.005
EDTA*	-	_	2.90	2.90	***	_
Na Citrate	-	_	-	_	2.90	2.90
APG	5.0	5.0	3.0	3.0	1.0	1.0
NaC12 Alkyl	1.95	_	1.95	_	1.95	_
benzene sulfonate						
NaC12 Alkyl	-	2.20	_	2.20	_	2.20
sulfate						
NaC12 (ethoxy)	_	2.20	_	2.20	Name -	2.20
**sulfate						

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C12 Dimethylamine	-	0.50	~	0.50	-	0.50
oxide						
SCS	1.30	_	1.30	_	1.30	-
Hexyl Carbitol**	6.30	6.30	6.30	6.30	6.30	6.30
Water and minors		В	alance	to 100	<b>ર</b>	

<sup>\*</sup>Na4 ethylenediamine diacetic acid

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### Example 18

The following spray composition for cleaning of hard surfaces and removing household mildew was prepared in accord with the present invention:

		I	
Amylase		0.0	)1
Specific lipolytic enzyme		0.0	)1
Protease		0.0	)1
APG		2.	0
Sodium octyl sulfate		2.0	00
Sodium dodecyl sulfate		4.0	00
Sodium hydroxide		0.8	30
Silicate (Na)		0.0	)4
Perfume		0.3	35
Water/minors	up	to	100%

<sup>\*\*</sup>Diethylene glycol monohexyl ether

<sup>\*\*\*</sup>All formulas adjusted to pH 7

#### What is claimed is:

1. A detergent composition comprising a lipolytic enzyme which provides a significantly improved whiteness maintenance performance over the Lipolase® enzyme when compared at an equal hydrolytic activity (same amount of LU per liter of wash solution) and an alkyl poly glucoside surfactant of the formula:

R-O-Gx

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- wherein R is on the average a  $C_{10}$  to  $C_{16}$ , preferably  $C_{12}$  to  $C_{14}$ , alkyl, G is a moiety derived from a reducing saccharide containing fron 5 to 6 carbons atoms, preferably a glucose unit, and x is on the average from 1.0 to 3.0 preferably from about 1.1 to 1.5, and represent the average degree of polymerisation of the alkyl polysaccharide surfactant.
- A detergent composition according to claim 1 wherein
   said lipolytic enzyme is present at a level of from 50LU to 8500LU per liter wash solution.
- 3. A detergent composition according to claims 1-2 wherein said lipolytic enzymes are variants of the native lipolytic enzymes producible by Humicola lanuginosa and Thermomyces lanuginosus, or by cloning and expressing the gene responsible for producing said variants into a host organism.
- 30 4. A detergent composition according to claim 3 wherein the lipolytic enzyme is a variant of the native lipase derived from Humicola lanuginosa strain DSM 4106.
- 5. A detergent composition according to claim 4 comprising the lipolytic enzyme variant D96L of the native lipase derived from Humicola lanuginosa.

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- 6. A detergent composition according to any of the preceding claims wherein said alkyl poly glucoside surfactant is a  $C_{12-14}O(glycosyl)_{1.3-2.7}$ .
- 5 7. A detergent composition according to any of the preceding claims wherein said alkyl poly glucoside surfactant is comprised at a level from 0.1 to 10%, preferably from 1 to 6%, more preferably from 2 to 5% by weigth of total composition.

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- A detergent composition according to any of 8. preceding claims further comprising one or more components selected from anionic, other nonionic, amphoteric and zwitterionic surfactants, cationic, builder, bleach system, suds suppressors, soil release polymer, lime soap dispersant, soil suspension and anti-redeposition agents, smectite clays and the like.
- 9. A detergent composition according to any of the preceding claims further comprising other enzymes providing cleaning performance and/or fabric care benefits.
- 10. A detergent additive comprising a specific lipolytic enzyme and an alkyl poly glucoside surfactant as defined in claim 1.
- 11. Use of a detergent composition according to claims 1-9 for hard surface cleaning and/or hand and machine dishwashing and/or hand and machine laundry cleaning.

# INTERNATIONAL SEARCH REPORT

Internal .1 Application No

			PC1/03 90/0/000						
A. CLASS IPC 6	SIFICATION OF SUBJECT MATTER C11D3/386 C11D1/66								
According	to International Patent Classification (IPC) or to both national cl	assification and IPC							
	B. FIELDS SEARCHED								
IPC 6	documentation searched (classification system followed by classif C11D	ication symbols)							
	tion searched other than minimum documentation to the extent th								
	data base consulted during the international search (name of data	base and, where practical, s	earch terms used)						
C. DOCUM	MENTS CONSIDERED TO BE RELEVANT								
Category *	Citation of document, with indication, where appropriate, of th	e relevant passages	Relevant to claim No.						
X	WO,A,96 12004 (THE PROCTER & GAMBLE CO.) 25 April 1996 see page 5 see page 12 see claims 1,6,7		1-11						
E	WO,A,96 16153 (THE PROCTER & GAI 30 May 1996 see example 4II	1-11							
Y	DE,A,43 15 854 (HENKEL KGAA. 17 November 1994 see page 2, line 52 - page 4, l see claims	) ine 7 -/	1-11						
▼ Furth	ner documents are listed in the continuation of box C.	N Permi familiano	and the same of th						
<u> </u>		X Patent family me	embers are listed in annex.						
'A' docume	begones of cited documents:  ent defining the general state of the art which is not erred to be of particular relevance document but published on or after the international	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention							
L' document which may throw doubts on priority claim(s) or which is cited to establish the publication data of mother		"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone.  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.							
later th	an the priority date claimed	"&" document member of	the same patent family						
	octual completion of the international search January 1997	Date of mailing of the international search report 29. 01. 97							
Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2  NL - 2280 HV Rijswijk  Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  Fax (+ 31-70) 340-3016		Authonzed officer  Serbetsoglou, A							

# INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/US 96/07088

CICARA	DOCUMENTS CONSIDERED TO BE BUILDED.	PCT/US 96/07088			
(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT  Regory * Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No.					
-wgur y	contains of document, with murcation, where appropriate, of the relevant passages	Relevant to claim No.			
Y	US,A,5 496 490 (BEAGLE CHARLES A. ET AL.) 5 March 1996 cited in the application see column 3, line 8 - line 61	1-11			
Y	GB,A,2 287 948 (THE PROCTER & GAMBLE CO.) 4 October 1995 see example 4	1-11			
Y	WO,A,92 05249 (NOVO NORDISK A/S ) 2 April 1992 cited in the application see claims 1-9,62-66; example 18	1-11			
A	RESEARCH DISCLOSURE, no. 359, 1 March 1994, EMSWORTH GB, pages 151-156, XP000440544 " 35944: DETERGENT COMPOSITIONS COMPRISING LIPASE VARIANTS" cited in the application see the whole document	1-11			
4	WO,A,94 14941 (BEROL NOBEL AB. ) 7 July 1994 see page 3, line 25 - page 4, line 27 see claims 1-6	1,6-11			
	·				

### INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat. Application No PCT/US 96/07088

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9612004	25-04-96	WO-A- AU-A- AU-A- WO-A-	9612000 1288195 3686995 9700929	25-04-96 06-05-96 06-05-96 09-01-97
WO-A-9616153	30-05-96	NONE		
DE-A-4315854	17-11-94	WO-A- EP-A- JP-T-	9426861 0698079 8510268	24-11-94 28-02-96 29-10-96
US-A-5496490	05-03-96	AU-A- CA-A- FR-A- NZ-A- ZA-A-	7144594 2131498 2709759 264313 9406446	23-03-95 08-03-95 17-03-95 26-04-96 26-02-96
GB-A-2287948	04-10-95	NONE		
WO-A-9205249	02-04-92	AU-B- AU-A- CA-A- EP-A- JP-T-	657278 8617291 2092615 0548228 6501153	09-03-95 15-04-92 14-03-92 30-06-93 10-02-94
WO-A-9414941	07-07-94	SE-A-	9203818	19-06-94